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***Evaluating an anaerobic digestion (AD) feedstock derived from a novel non-source
segregated municipal solid waste (MSW) product***

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feedstock, sustainable biogas production; regulation of waste

Abstract

In many nations industrial scale AD of non-agricultural waste materials (such as MSW) has not yet reached its full potential, often constrained by the lack of secure, inexpensive, high quality AD feedstocks, and markets for the resulting digestate material. We tested the output material of a high throughput novel industrial process to define its potential as an AD feedstock (based on quality and consistency). This process, designed to circumvent the constraints of source segregation while still generating segregated waste streams, resulted in the production of a temporally homogenous fibrous material with: an average moisture content of $44.2 (\pm 2.33) \%$; C: N ratio of $\sim 32.9:1 (\pm 3.46:1)$, C: P ratio of $\sim 228:1$ and gross calorific value of $17.4 (\pm 0.29) \text{ MJ/kg}_{(\text{DM})}$. This material provided a CH_4 yield of between 201 and $297 \text{ m}^3 \text{ CH}_4 / \text{tonne}_{(\text{DM})}$ ($271 - 401 \text{ m}^3 \text{ CH}_4 / \text{tonne}_{(\text{vs})}$) comparable to commonly used AD feedstocks. Material contaminant levels were temporally consistent ($P > 0.05$), (average values being Cd $0.63 (\pm 0.19)$, Cu $56.3 (\pm 7.45)$, Cr^{tot} $51.4 (\pm 4.41)$, Hg < 0.3 , Ni $28.9 (\pm 5.17)$, Pb $79.2 (\pm 23.71)$, Zn $202 (\pm 44.5)$, total polyaromatic hydrocarbons (PAH) $2.2 (\pm 0.3)$, and total polychlorinated biphenyls (PCB) (< 0.2) $\text{mg/kg}_{(\text{DM})}$). Calculated digestate contaminant levels were below the median contaminant threshold limits for anaerobic digestates of all countries within the European Union i.e. of Cd 3.35, Cu 535, Cr^{tot} 535, Hg 8.15, Ni 185, Pb 397.5, Zn 2100 $\text{mg/kg}_{(\text{DM})}$). We suggest that novel high throughput processes that produce high quality AD feedstocks, may have a place in further diversion of waste from landfill.

1. Introduction

Although 84% of MSW is collected globally, only 15% is currently recycled (Zaman, 2016) and, regardless of country income, landfilling is the predominant disposal route (Zaman, 2016). Although the European Directive on Landfill of Waste (European Commission, 1999)

44 has reduced the disposal of biodegradable municipal waste to landfill (Bulkeley et al., 2005;
45 Edwards et al., 2015) a wide variation (5 to 80%) in diversion rates still exists amongst
46 member states (European Commission, 2015). The European Commission is currently
47 developing a long term vision to address this disparity (European Commission, 2015),
48 however, in countries where diversion of biodegradable waste from landfill has increased
49 from a low baseline such gains have more recently reduced or plateaued. For instance, the
50 UK increased diversion from 11% in 2000-2001 to 43.2% in 2011-2012 (DEFRA, 2012),
51 however, the rate of progress has reduced year on year since 2005 and from 2012 to 2013
52 the diversion rate only increased by 0.3% (DEFRA, 2013). Often source-segregation is
53 advocated as a 'key to the success' in non-landfill waste management systems (Yang et al.,
54 2016), but, success is determined by the complex interplay of environmental, economic, and
55 social factors (Di Maria et al., 2016; Tavares et al., 2009; Rispo et al., 2015; Bulkeley &
56 Gregson, 2009) interacting within changing governance and political systems (Bulkeley et al.,
57 2005). Interestingly, Rispo et al., (2015) has suggested that that source-segregation may be
58 particularly challenging within hard to reach high density urban communities. We suggest
59 that to realise a 'resource efficient, circular economy' where biodegradable waste becomes
60 a valued resource (DEFRA, 2015; European Commission, 2015), novel and diverse
61 approaches to municipal waste management will be essential including where source-
62 separation is not favoured, practicable, or financially viable (DEFRA, 2013).

63 Biogas production from 'waste products' by Anaerobic Digestion (AD) is often described as
64 an environmentally sympathetic, and economic method of fuel and 'nutrient-rich fertiliser'
65 generation (Bolzonella et al. 2006; DEFRA, 2010; Tambone et al. 2010; Di Maria et al. 2013;
66 Massaccesi et al. 2013). AD is, therefore, an important means (Frick, Santen and Wallmann,

2005) of addressing the interconnected issues of: sustainable waste management (European Commission, 1999; Edwards et al., 2015); renewable energy provision, and; 'stabilisation of greenhouse gas (GHG) emission rates' (UNFCCC, 1997; Beurskens et al., (2011)). However, slow adoption of AD within non-agricultural settings is often attributed to availability of high quality secure feedstocks, and limited potential to develop economically and environmentally sustainable markets or disposal routes for the resulting digestates (Brooks and Maxwell-Jackson, 2012; WRAP, 2013a; Bulkeley et al., 2005) which are governed by regulatory requirements at both broad international and specific national levels (Saveyn and Eder, 2014). Critically, a common feature of compliance for primary waste feedstocks is their segregated at source (WRAP, 2011; Saveyn and Eder, 2014). Feedstocks produced from non-source segregated materials may require extensive pre-treatments, produce lower or variable biogas yields, and also require more intensive post treatments of liquids and solids discharged from the reactors (Di Maria et al. 2012); all of which will require additional investment and have higher operational costs.

Since the 1990's there has been increasing interest in development and introduction of industrial scale MSW processing facilities aimed at enhancing the recovery and reuse of high value materials from non-source segregated MSW (e.g. Mechanical Biological Treatment) (De Gioannis, G., 2009; Monteo et al., 2013). A number of these processes include stabilisation of biodegradable materials, through composting or AD, as a stage within a sorting and separation process (Fricke et al., 2005) e.g. SORTing- DIgestion- SEPeration (SORDISEP) (Torfs et al., 2005). In parallel, in the last 25 years, autoclaving has gained interest as a mechanism for the treatment of clinical solid waste, household waste, and non-source segregated MSW (e.g. DEFRA 2013; Garcia et al., 2012), and it is thought that this process may be applied further e.g. to the rejected fractions of mechanical biological treatment (MBT) to maximise recycling

rates (Garcia et al., 2012). Autoclaving is a hydrothermal high pressure treatment process (from temperatures of 121°C to 145°C and pressures of up to 3 Bar) routinely used in the decontamination of infectious lab waste, clinical and dental tools. Autoclaving is less physically aggressive than steam explosion which is typically carried out at higher temperatures (of 160°C - 260°C) and pressures (of 6.9 – 48.3 Bar), and which are accompanied by a rapid pressure release (e.g. 20 seconds duration) which aids material transformation e.g. in wood products (Teghammar et al., 2010; Vochozka et al., 2016).

With regard to treatment of mixed household and MSW, autoclaving has been shown to have the potential to reduce the initial volume of waste (through maceration and compaction; Garcia et al., 2012), which if combined with post autoclave material segregation can divide recyclable materials into separate fractions (i.e. glass, plastic, ferrous metals, non-ferrous metals, textiles), and result in the production of a single unified organic material product (Garcia et al., 2012). To date studies of this treatment method have often been carried out using synthesised waste materials, at relatively small lab, or pilot, scale (Houltman et al., 2016; Papadimitriou et al., 2008; Papadimitriou, 2010). Within this study we use a full capacity industrial scale rotational autoclave (roto-autoclave) process as a model system for the production of an AD feedstock from non-source segregated MSW. The aim of this study was to assess both the quality and consistency of this fibrous material produced in this process: in terms of physical, chemical and biological attributes, and to compare these with commonly used anaerobic digestion feedstocks, and with existing regulations.

2. Methods

2.1. Processing

The industrial process was run at full capacity utilising local authority derived MSW for 10 consecutive days. Successive non-sorted batches of the MSW (12 x 20 tonne batches in a 24 hour period) were treated by roto-autoclaving, at 140°C for 45 minutes at a maximum

pressure of 3 bar before depressurisation and cooling (20 minutes). This process was followed by extensive semi-continuous mechanical separation which included an initial finger screen which removed large items (>200mm), followed by; air separation, magnets, eddy current separators, optical sorters, glass separators, and a manual picking station (to remove further textiles, and large items). This produced 6 distinct waste streams – glass, plastic, ferrous metals, non-ferrous metals, textiles, and a fibrous material (diameter \leq 12 mm). A waste stream mass balance was not conducted during this trial as the focus was exclusively on the fibre output.

A composite sampling protocol was carried out based on ASTM D5956-96 (2006) and ASTM D6051-96 (2015) for fibre analysis (rather than using sorting based methods usually applicable to MSW e.g. ASTM D5231-92 (2008)). Samples were obtained at the final point of mechanical separation whereby 8.5 kg of the fibrous material (\leq 12mm) was collected at intervals of 2 hrs for 24 hrs (in a large covered receptacle). Each 24 hr period was classified as 1 sampling day (there were 10 consecutive sampling days). After the 24 hr period, the resulting material (102kg) was thoroughly mixed and divided using coning and quartering (ISO 23909, 2008) and 25 kg of the resultant homogenised bulk sample was divided into distinct aliquots which were either refrigerated (4°C), frozen (-80°C), or dried (at 105°C) for down-stream analysis (outlined in Sections 2.2 – 2.6). The storage, preservation and processing times of samples was dictated by the downstream methods used (Sections 2.2.- 2.6).

2.2. Characterisation

The fibrous material was analysed for Cd, Cr, Cu, Hg, Ni, Pb, Zn (BS EN 15297, 2011), total N,C,O,S,H (BS EN 15104, 2011), calorific value (BS EN 14918, 2009), moisture content (BS EN

15414-3, 2011), total Kjeldahl nitrogen (TKN) using a Gerhardt reflux and distillation system (Gerhardt, Germany; BS EN 16169, 2012), weight loss on ignition at 550°C (LOI₅₅₀ which is equivalent to VS), total poly-aromatic hydrocarbons (PAH i.e. sum of 16 US Environmental Protection Agency commonly tested PAH; BS EN 15527, 2008), total polychlorinated biphenyls (PCBs) (BS EN 15308, 2008), microbial pathogen indicator organisms i.e. *E.coli* (ISO 11866-2, 2005; using a colony-count technique at 44°C) and *Salmonella* (ISO 6579, 2002; using the horizontal method), biogas production potential (Sections 2.3 and 2.4), material structure analysis (Environmental scanning electron microscopy (ESEM; Section 2.5), and carbon characterisation (Fourier Transform Infrared spectroscopy (FTIR), and thermogravimetric differential scanning calorimetry (TG-DSC) analysis; Section 2.6).

2.3. AD batch system set up and gas analysis

Samples from each of the 10 sampling days were set up in triplicate, in 120 ml Wheaton serum bottles, using a 3% dry solid content (the liquid component was made up of a 1:1 ratio of deionised water: acclimatised anaerobic sludge inoculum, and the ratio of inoculum to fibrous material (dry mass) was 15:1). Additionally, a triplicate inoculum only blank was used. The inoculum was obtained from a thermophilic Continuous Stirred Tank Reactor (CSTR) previously optimised for this material (operated for > 80 days at 50°C, 10 % solids and 20 days hydraulic retention time) and stored at 4°C (for 1 month) until use in batch systems. This storage time has been shown to be applicable to bio-methane production potential (BMP) tests by Hagen et al., (2015). Serum bottles were sealed and headspace gas displaced with oxygen free nitrogen to ensure anaerobic conditions. Samples were incubated under thermophilic conditions (50°C) for a total of 57 days to gain the information captured during 30 day BMP tests, and furthermore to allow biogas production plateau to be achieved. Excess headspace gas was removed and quantified regularly, using a

graduated 100 ml gas tight borosilicate syringe (Sigma, UK). To measure the headspace gas composition 100 µl aliquots of microcosm gas were taken in a nitrogen-flushed gas-tight push lock syringe (Hamilton, UK), and the methane content determined by gas chromatography using a Flame Ionisation Detector (Chi Fru et al., 2011). Gas composition was quantified on the basis of peak area, calibrated using standards within the linear range (Scientific & Technical Gases Ltd, UK).

To determine if post roto-autoclave physical or chemical treatment of the fibrous material could further enhance BPP, a further batch of fibrous material was (in triplicate) treated with either 1% (w/v) HCl, or 1 % (w/v) NaOH, with ultrasound (42,000 Hz, 200 W, 24hrs) (Clifton MU-14 Ultrasonic bath; Progen Scientific, UK), and compared to a roto-autoclaved control. Where appropriate the treated materials were then adjusted to pH 7 and dried to 105°C, and were then set up, and monitored as above.

2.4 Continuous Stirred Tank Reactor (CSTR) set up and analysis

A CSTR was setup using a 6 L Quick-fit reactor vessel (5 L working volume), immersed in a water bath, and was maintained at 50°C for the duration of the experiment. A Quick-fit flanged, multi-port head-plate was fitted to each reactor with a spring-clamp. Five 19/26 ground glass-sockets on the head-plate allowed for continuous biogas gas production monitoring and periodic feedstock addition and digestate removal. In addition, an impeller drive shaft was fitted to the reactor through a glass stirrer gland with water-seal. Unused inlets were sealed with ground glass 19/26 stoppers. Continuous mixing was achieved with a 40 x 80 mm rectangular impeller rotating at 200 rpm. Vacuum grease (Dow Corning, USA) was used to maintain the integrity of all ground glass seals. The reactor was inoculated with a mixed methanogenic sludge obtained from a previous CSTR study on the AD digestion of

this specific feedstock material (as per Hinks et al., 2013), as such the inoculum was pre-adapted to this system. This was the same inoculum used in the batch tests. The CSTR was operated in a semi-continuous mode and was fed daily with 17 g_(DM) (equivalent to 7% solids, 3.4 kg_(DM) / m³_(reactor volume) / day or, 2.52 kg_(VS) / m³_(reactor volume) / day) for 41 days. The hydraulic retention time was 20 days. Biogas production rates were measured using commercial bubble counters, (AER-208 Respirometer, Challenge Technology, Arkansas USA) with real-time data recording by desktop PC. Additionally, biogas was collected periodically for CH₄ analysis directly from the reactor biogas line in evacuated 3.7 ml glass vials (Labco, UK) and analysed as described above in Section 2.3. pH of removed digestates was determined using a handheld pH probe (Hanna instruments, UK). Digestate total solids were determined in triplicate (dried at 105°C until constant weight, and the TS expressed in g.L⁻¹). Total volatile solids (VS) were determined after ignition of dried solids at 550°C. Total dissolved organic carbon was determined on digestate filtrates (0.45 µm) using Shimadzu 5050A Total Organic Carbon Analyser, with an ASI-5000A automatic sampler (Shimadzu, Germany).

2.5 Material micro-structure

Environmental scanning electron microscopy (ESEM) was carried out by the Advanced Chemical and Materials Analysis facility, Newcastle University, using a FEI XL 30 Environmental scanning electron microscope attached to a field emission gun (ESEM-FEG; Philips). Samples were air dried and analysed under a low vacuum using an acceleration voltage of 10 kV and magnification of x 250 to x 6500.

2.6 Characterisation of organic carbon composition in feedstock and digestate

TG-DSC and FTIR were carried out to characterize carbon composition. They were carried out on pre- and post- AD digestion samples that were dried at 105°C overnight and then cryogenically ground (cooled under liquid nitrogen for 3 minutes and then ground for 2 x 1 minute periods at a speed of 10 rps; Spex mill 6750 freezer mill, Thermo Fischer, UK).

TG-DSC was carried out using a 30 mg sample (Netzsch Jupiter STA 449C instrument with helium/oxygen (80%/20%) as the carrier gas mix flowing at 30 ml/minute for a heating cycle from 30-900°C at a ramping rate of 10°C/minute) (Lopez Capel et al., 2006). DSC outputs were used to define the boundary temperature ranges which could be attributed to the labile and refractory organic carbon components of the samples in the TG mass loss curves (Lopez Capel et al 2005; Fernandez et al., 2012). These labile and refractory organic carbon components have been shown by Lopez Capel, (2005) to correspond to the cellulose-like, and lignin-like components of soil organic matter. In the pre-AD material the putatively cellulosic component range between 260°C and 440°C, and the putatively ligninic component range between 440°C and 600°C. Post-AD the putatively cellulosic range was between 260°C and 400°C, and putatively ligninic between 400°C and 600°C. The fixed solids content was defined in this study as the residual mass obtained after combustion at 600°C. The TG mass loss assigned to putatively cellulosic material component range (between 260°C and 440°C) of pre-AD material was used to calculate a theoretical maximum methane production based on breakdown of cellulose to methane.

FTIR was carried out on pressed pellets (Specac press; Smiths, UK) prepared from 4 mg ground dried sample mixed with 200 mg of FTIR grade KBr (Sigma, UK). Samples were measured over the mid infrared range (4000 - 400 cm⁻¹) using a Nicolet 6700 FTIR in

transition mode attached to an In GaS detector (Thermo Scientific, UK). Spectral resolution was set at 4cm^{-1} , and 32 scans were recorded, averaged and corrected against a KBr only background.

3. Results

3.1. Quality and Consistency of fibrous material

The process of roto-autoclaving produced a visually homogeneous material, which was confirmed as free of pathogen indicator organisms typically present in untreated MSW (i.e. *Salmonella* (< 10 C.F.U/ 25g material) and *E.coli* (< 10 C.F.U /g material). Subsequent mechanical separation produced segregated waste streams including the fibrous material. This fibrous material, as received, had an approximately neutral pH (average $7.1 (\pm 0.25)$), an average moisture content of $44.2 (\pm 2.33) \%$, C: N ratio of $\sim 32.9:1 (\pm 3.46:1)$; Table 1), C:P ratio of $\sim 228:1 (\pm 18.6)$ and an average gross calorific value of $17.4 (\pm 0.29) \text{ MJ / kg}_{(\text{DM})}$. These measured variables were consistent both within and between sample batches (one-way ANOVA $p > 0.05$). Regression analysis was used to explore temporal change (over the 10 day sampling period). No temporal component was identified in material properties within the sampling period (regression analysis $p > 0.05$, Table 1).

Analysis of the material's structure by SEM indicated that it comprised distinct but intertwined fibres (approximately $1500 \mu\text{m} \times 16 \mu\text{m}$). These fibres (Figure 2) were structurally similar to partially hydrolysed cellulose, as shown in Li et al., (2012). The carbon composition of this material was investigated further using qualitative (FTIR) and quantitative analysis methods (TG-DSC). The FTIR absorbance spectra (from $4000 - 400 \text{ cm}^{-1}$) included a broad band between 3400 and 3500 cm^{-1} which can be attributed to bonded and non-bonded hydroxyl groups (Fernandez et al., 2012), and a number of characteristic

cellulose, hemicellulose and lignin band wavelengths; including those at 1170 cm^{-1} (cellulose), $1700 - 1740\text{ cm}^{-1}$ and $1230 - 1260\text{ cm}^{-1}$ (hemicellulose), and $1505 - 1515\text{ cm}^{-1}$ (lignin) (Smidt and Schwanninger, 2005; Figure 2).

Average DSC profiles were used to define boundaries for the thermal mass loss (TG) attributed to the putatively cellulosic material (labile carbon which we recognise may also include a small component of aliphatic compounds as simple lipids and amino acids, consequently associated with the most easily-degradable fraction of the organic matter), putatively ligninic material (refractory carbon including aromatic compounds or other polyphenols, distinctive of a more humified and stable fraction of the organic matter), and the fixed solids (residual mass component) (Fernandez et al., 2012) (Figure 3). The novel organic feedstock material had a putatively cellulosic material content of $55.9 (\pm 1.31)\%$ based on mass loss over the temperature range 260°C to 440°C , a putatively ligninic carbon content of $11 (\pm 0.49)\%$ based on mass loss over the temperature range 440°C and 600°C (Figure 3), and a fixed solids component $23.2 (\pm 1.15)\%$. In contrast, digestate had a putatively cellulosic material content of $31.4 (\pm 3.2)\%$ based on mass loss over the thermal range of 260°C to 400°C , putatively ligninic content of $20 (\pm 0.44)\%$ based on mass loss over the thermal range of $400^{\circ}\text{C} - 600^{\circ}\text{C}$, and a fixed solids content of $42.7 (\pm 0.60)\%$ (Figure 3). Normalising the mass loss of putatively cellulosic and ligninic carbon fractions to the fixed solids component indicated that the process of anaerobic digestion removed, on average, 54.4% of the total biomass. It should be noted from these profiles that AD predominantly removed material and energy value from the low temperature combustible component i.e. putative cellulose content (Figure 3).

In terms of contaminants, a selection of heavy metals common to European AD threshold standards (Cd, Cr, Cu, Hg, Pb, and Zn) were analysed to indicate the presence and variance of inorganic contaminants, along with total PAHs (16 EPA) and total PCBs to indicate the presence and variance of organic contaminants. Low levels of the heavy metals Cd, Cr, Cu, Pb, Ni and Zn were identified in all batches of the material (Table 1), average values being Cd 0.63 (\pm 0.19) mg/kg_(DM), Cu 56.3 (\pm 7.45) mg/kg_(DM), Cr^{tot} 51.4 (\pm 4.41) mg/kg_(DM), Hg <0.3 mg/kg_(DM), Ni 28.9 (\pm 5.17) mg/kg_(DM), Pb 79.2 (\pm 23.71) mg/kg_(DM), Zn 202 (\pm 44.5) mg/kg_(DM). In all instances metal levels were consistent across temporally sampled batches (regression analysis $p > 0.05$; one-way ANOVA $p > 0.05$). Levels of Hg remained below the detection limits (below 0.3 mg/kg_(DM); Table 1). Similarly, total PAH levels were low (average 2.2 (\pm 0.3) mg/kg_(DM)), (regression analysis $p > 0.05$), while total PCBs remained below detection limits (below 0.02 mg/kg_(DM)).

3.2. Biogas production potential and organic carbon transformation of in batch microcosms

In batch microcosms systems (50°C) biogas accumulation followed a similar pattern for each sample. Initially a rapid accumulation of biogas volume occurred between days 1 and 10 followed by a progressively slower accumulation of biogas, until the maximum yield (of between 424 and 541 m³ biogas volume/tonne_(DM)) was achieved (Figure 4). In all instances, 90% of the final biogas yield was reached by 21 days. The methane composition of the biogas reached a maximum of between 51 to 62% v/v from day 14 onwards. After 31 days the methane production plateaued at between 201 and 297 m³ CH₄/tonne_(DM), 271 -401 m³ CH₄ /tonne_(VS) (Figure 4). Over the course of the experiment no significant differences were apparent in methane production potentials (one - way ANOVA, $p = 0.941$ at T0, and $p =$

0.380 at 49 days incubation). In each instance the observed plateaued methane production potential was close to the average theoretical maximum methane production for the system, of $223 (\pm 5.26) \text{ m}^3 \text{ CH}_4 / \text{tonne}_{(\text{DM})}$ (and $299 \text{ m}^3 \text{ CH}_4 / \text{tonne}_{(\text{VS})}$). This theoretical maximum was based simply on the maximum putatively cellulosic carbon component determined from TG-DSC analysis. Further treatment of the fibrous feedstock material with acid, alkali or ultrasound before anaerobic digestion did not enhance methane yields (one - way ANOVA, $p = 0.560$).

3.3. Biogas production in a Continuous Stirred lab-scale reactor (CSTR) operated under thermophilic conditions

At a loading rate equivalent to $3.4 \text{ kg}_{(\text{DM})} \text{ m}^{-3}_{\text{reactor volume}} \text{ day}^{-1}$ ($2.52 \text{ kg}_{(\text{VS})} / \text{m}^3_{\text{reactor volume}} / \text{day}$) for a period of two hydraulic residencies biogas production reached $324 (\pm 37) \text{ m}^3_{\text{biogas}} \text{ tonne}_{(\text{DM})}^{-1} \text{ day}^{-1}$; $438 (\pm 50) \text{ m}^3_{\text{biogas}} \text{ tonne}_{(\text{VS})}^{-1} \text{ day}^{-1}$; $1.01 (\pm 0.12) \text{ m}^3 \text{ m}^{-3}$ (Figure 5a) which, based on an average methane content of $61.3 (\pm 1.4)\%$, equated to $198 (\pm 23) \text{ m}^3 \text{ CH}_4 \text{ tonne}_{(\text{DM})}^{-1} \text{ day}^{-1}$; $267 (\pm 31) \text{ m}^3_{\text{biogas}} \text{ tonne}_{(\text{VS})}^{-1} \text{ day}^{-1}$). This production rate which was equivalent to between 60 - 77% of the empirically determined maximum yields based on data from batch digestion assays. During CSTR operation, the DOC, total solids (TS) and total volatile solids (VS) contents (Figure 5b and C) all followed similar trends with, for example, a drop of the total solids content from 34.3 g/L (reflecting the inoculum composition) to a final value of 16.7 g/L after two hydraulic residencies. The pH of the CSTR started at above 7.5 but progressively dropped over the 40 days to 6.73.

4. Discussion

4.1. Bulk Characteristics

The composition of untreated municipal solid waste is known to be extremely heterogeneous, as such its composition is predominantly 'deemed' visually, rather than characterised by physical or chemical analysis (ASTM D5231-92, 2008). In contrast to MSW the visual and physical composition of the novel fibrous material presented in this study was both spatially and temporally homogenous (over the trial period) at the macro and micro-scale (Figure 2). Similarly, in contrast to unprocessed source separated OFMSW or MSW samples which have a variety of microorganisms including pathogens present (Sundberg et al., 2011), the novel fibrous material was shown to be free of pathogen indicator organisms i.e. *Salmonella* and *E.coli* after undergoing the roto-autoclave process.

Below we compare bulk fibrous material characteristics with studies which characterise processed OFMSW (Hansen et al., 2007; Davidsson et al., 2007) and to a recent review of global OFMSW characteristics carried out by Campuzano & Gonzalez-Martinez, (2016). This comparison is made also because the fibrous material is often thought of as most akin to the processed organic fraction of municipal solid waste (OFMSW), defined by Alibardi & Cossu (2015) as being predominantly composed of fruit and vegetable materials. However the fibrous material is not necessarily restricted to the constituents of OFMSW and may potentially include a much wider range of organic materials including paper, cardboard, nut shells, kernels, and bones as constituents.

OFMSW has the average global pH of 5.2 (± 0.95), moisture content of 72.8 (± 7.6) %, TS 27.2 (± 7.6) % and VS of 84.6 (± 9.9) % (Campuzano & Gonzalez-Martinez, 2016). In comparison our fibrous material displays a higher neutral pH 7.1 (± 0.25), far lower moisture content 44.2 (± 2.33) %, far higher TS of 55.8 (± 2.33) %, and comparable VS of 74.1 (\pm

4.06) %. Further elemental composition analysis of dry mass indicates the global range of OFMSW for C of 46.6 (± 4.4) %, H 6.6 (± 0.62) %, N 2.9 (± 0.6) % and S 0.3 (± 0.26) % (Campuzano & Gonzalez-Martinez, 2016). Our fibrous material contains lower proportions of C, H, and N than OFMSW, but comparable levels of S (Table 1). Hansen et al., (2007) found that the average gross calorific value of OFMSW was between the range of 19.7 to 20.8 MJ/ kg_(DM) , which is slightly higher than the average of 17.4 (± 0.29) MJ /kg_(DM) outlined for the fibrous material. This comparison between global OFMSW and the novel fibrous material indicates that in terms of chemical and elemental characteristics there are similarities i.e. in VS, and calorific value, but that for most chemical and elemental variables the fibrous material sits slightly outside the stated global ranges of OFMSW. Making a wider comparison with common AD feedstocks, the C:N ratio of $\sim 32.9:1$ (95% CI ± 3.46) outlined for fibrous waste is similar to the upper ratio of food waste e.g. range of 14.8:1 to 36.4:1 (Zhang et al., 2007), higher than OFMSW (range from 15.5- 28.2:1) (Massaccesi et al., 2013; Hansen et al., 2007; Davidsson et al., 2007), green waste and mixed waste composts (range of C:N 13-17: 1) (Tambone et al., 2010), and Cattle slurry (20:1) (Macias-Corral et al., 2008).

4.2. Biogas production potential

When the methane production potential of the fibrous material (i.e. 201 to 297 m³ CH₄/tonne_(DM)) was compared with commonly used AD feedstocks, it was shown to be similar to low fat food waste, source segregated MSW, and to meadow grass, which have methane production potentials of between 214 and 294 m³CH₄/ tonne_(DM), but lower than high fat food wastes, sugar beet, and maize which had a methane production potential of between 300 and 450 m³ CH₄/ tonne_(DM) (Table 3). When biogas production potential was assessed and compared with the other materials as received (AR) this novel organic material is seen to have a far greater methane production potential per unit mass (AR) due

to its lower intrinsic water content (Figure 6). This lower intrinsic water content is undoubtedly favourable from both an economic and logistical standpoint i.e. removing any additional energy requirement in terms of drying and minimizing transport costs. In their 'As received' forms the AD production potential of the fibrous material is bettered only by rice straw (Figure 6), which, although one of the most important agricultural wastes in China (Yong et al., 2015) is not a major component of the potential AD feedstocks within the geographic region of this study (i.e. Europe). In contrast when the methane production potential of the fibrous material is compared with others normalised to volatile solids, the range of 271 to 401 m³ CH₄/tonne_(vs) is within the broad global range of OFMSW, food waste, meadow grass and rice straw (of 298 to 600 m³ CH₄/tonne_(vs)), and is higher than dairy cow slurry (i.e 161 m³ CH₄/tonne_(vs)).

In the lab scale CSTR study of the fibrous material, high percentage yields of biogas were consistently produced relative to the maximal biogas potentials determined empirically for this feedstock (Figure 5). The semi-continuous nature of the feeding regime would lead to daily fluctuations of undigested solids above the average solids content. Despite this the reactor showed consistent performance and relative stability (Figure 5). In combination, these factors indicate the robust nature of this material as an AD feedstock.

4.3. Inorganic and Organic contaminants

As the novel fibrous material was produced from non-source segregated MSW, it is anticipated that bulk and chemical contaminants present within the MSW may become incorporated within the material during the process of roto-autoclaving, and remain after subsequent mechanical separation procedures (Papadimitriou et al., 2008). There are numerous potential sources of heavy metals within MSW, e.g. batteries, paints, electronics,

ceramics, plastics and inks/dyes (Richard and Woodbury, 1992; Sharma et al., 1997; Slack et al., 2004). Despite the source potential for contamination, heavy metal concentrations in the fibrous material (average values Cd 0.63 (\pm 0.19), Cu 56.3 (\pm 7.45), Cr^{tot} 51.4 (\pm 4.41), Hg <0.3, Ni 28.9 (\pm 5.17), Pb 79.2 (\pm 23.71), Zn 202 (\pm 44.5) mg/kg_(DM)), were generally lower than those measured in household floc material (Papadimitriou et al, 2008), comparable with the median worldwide soil heavy metal contents outlined in Smith, (2009), but higher than autoclaved food waste (e.g.Ibrahim et al., 2011) (Table 3).

Based on the average reported mass reduction after anaerobic digestion (calculated from TG analysis of batch AD experiments as 54.4 %) it was possible to make an estimate of the heavy metal content of the digestate (average calculated values Cd 1.4, Cu 123.5, Cr^{tot} 112.7 , Hg <0.3, Ni 63.4, Pb 173.7, Zn 443 mg/kg_(DM)) (Table 2). This conservative approach did not take into consideration partitioning of metal compounds between liquid and solid phases during digestion (Chen et al., 2008; Swanwick et al., 1969) at the pH range of the digestate, and thus the potential subsequent removal of water soluble compounds by commonly used dewatering processes. Nevertheless, assuming all metals to partition into the solid fraction of the digestate, the average calculated metal concentrations in the digested fibrous material was found to be comparable to studies of MSW-derived AD feedstocks (Table 2), and were close to the threshold limits of conservative national requirements for anaerobic digestates e.g. UK (Cd 1.5, Cu 200, Cr^{tot} 100, Hg <1, Ni 50, Pb 200, Zn 400 mg/kg_(DM)), and below the calculated median of EU-wide standards for heavy metal thresholds for anaerobic digestate (Cd 3.35, Cu 535, Cr^{tot} 535, Hg 8.15, Ni 185, Pb 397.5, Zn 2100 mg/kg_(DM))(Table 2).

The production of novel materials from mixed waste streams can lead to a high degree of uncertainty about contaminants present within the ultimate products, and will not necessarily be limited to the commonly tested inorganic contaminants above, which are based on regulatory threshold requirements. Current regulation of anaerobic digestate does not generally indicate upper threshold limits for organic contaminants. For example, WRAP (2011) states that the controls placed on feedstock materials, i.e. source segregation, are 'perceived to be sufficient to protect the quality of the digestate'. However, to provide comparison, PAH levels in the current study (average 2.2 ± 0.30 mg/kg) were below the European proposed limits for total PAH in sewage sludge (6 mg/kg), and were similar to digested source segregated food wastes (WRAP, 2011). Similarly total PCB levels were below detection levels (of 0.02 mg/kg). Other noteworthy materials for future studies of MSW derived AD feedstocks include personal care products, pharmaceuticals, flame retardants, nanoparticles (Albero et al., 2015), some plastics and associated compounds (North and Halden., 2013), and heat resistant biological contaminants (e.g. prions). We suggest that any future changes to the current regulatory system, that would allow wider use of non-source segregated MSW derived materials, should be based on the quality and consistency of MSW derived material (a risk based approach), rather than the exclusion principle (requirement for source segregation). It is also essential that the potential contaminants mentioned above, and their derivatives, are investigated within representative model systems such as the one outlined in this study.

4.4. Wider potential relevance of this waste treatment process

In the current study we have identified a need for EU-wide harmonisation of voluntary and statutory standards for waste products (e.g. anaerobic digestates) based on the actual

quality and consistency of materials, rather than on the exclusion principle (applied to non-source segregated waste derived products), and suggest that this will aid both environmental protection and the move towards a circular economy where solid waste becomes a valued resource. Assuming this eventuality, the novel standalone process evaluated in this study could potentially divert ~3% of the UK's non-source segregated MSW from landfill (based on the 10.4 million tonnes of non-source segregated MSW disposed of to landfill in the UK in 2011/2012 (DEFRA, 2012)). If extended, in the first instance nationally, this could produce a maximum of 6.76 million tonnes of AD feedstock (DM) per annum. The business case for roto-autoclaving and separation of MSW was based on the overall reduction in MSW volume, combined with the separation, and diversion of recyclates from landfill. However, it is particularly convenient that the resulting biodegradable material may also be utilised as an AD feedstock. Assuming the energy yield from the produced biogas is obtained from the methane fraction, a reference calorific value of methane of $36 \text{ MJ} / \text{m}^3$ is multiplied by the minimum and maximum CH_4 production indicated by batch assays of 201-297 $\text{m}^3 / \text{tonne}_{(\text{DM})}$ to give a theoretical range of between $(36 \times 201) = 7236 \text{ MJ} / \text{tonne}_{(\text{DM})}$ to $(36 \times 297) = 10692 \text{ MJ} / \text{tonne}_{(\text{DM})}$. Using $1 \text{ Wh} = 3600 \text{ J}$, this is 2.01 - 2.97 MWh / $\text{tonne}_{(\text{DM})}$. Given an annual feedstock availability of 6.76 million tonnes $_{(\text{DM})}$, this indicates a potential energy yield of 13.6-20.0 TWh p.a., although the parasitic energy inputs (for pumps and heating) must still be subtracted to give the final balance. To contextualise this figure, natural gas production in the UK was 460 TWh in 2015 (Department for Business, Energy and Industrial Strategy, 2016).

In addition to this energy yield, the process would produce an average of 3.1 million tonnes of digestate. Monlau et al., (2015), state that it is possible that the market for anaerobic digestate will extend beyond land use into sectors such as microalgae cultivation, further

biological biofuel production, and thermo-chemical energy production to ensure optimal conversion and energy recovery. Inclusion of these options for digestate use could truly provide an environmentally and economically flexible means creating a resource efficient circular economy with close to zero waste.

5. Conclusion

Within the current EU regulatory landscape, tension exists between protecting the environment, and supporting the development of innovative approaches to waste management. We suggest that use of non-source segregated MSW derived products (produced by autoclaving and mechanical separation) could effectively divert large volumes of mixed waste from landfill, while producing secure, high quality feedstocks for biogas production. We have described a novel homogeneous non-source segregated MSW AD feedstock which:

- Has low intrinsic levels of toxic inorganic and organic contaminants;
- CH₄ yields comparable to other commonly used AD feedstocks (i.e. 271 – 401 m³ CH₄ / tonne_(VS));
- Is logistically favourable due to its low intrinsic moisture content (AR);
- Could potentially divert high volumes of non-source segregated MSW from landfill.

However before this process can be replicated at large scale nationally and internationally, further development of economically and environmentally viable markets for the resulting digestate (e.g. in land use or thermo-chemical energy production) will be required. This may require harmonisation of EU threshold standards with regard to feedstock quality.

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Highlights

- Recycling of MSW may depend on inclusion of novel approaches to waste management
- A novel homogenous non-source segregated MSW AD feedstock was produced
- CH₄ yields similar to other common feedstocks in terms of total and volatile solids
- Due to low moisture contents CH₄ yields were high in terms of as received mass
- Digestate contaminants were below the median European threshold limits
- Future use of such AD feedstocks and digestates requires harmonisation of regulation

Figure 1

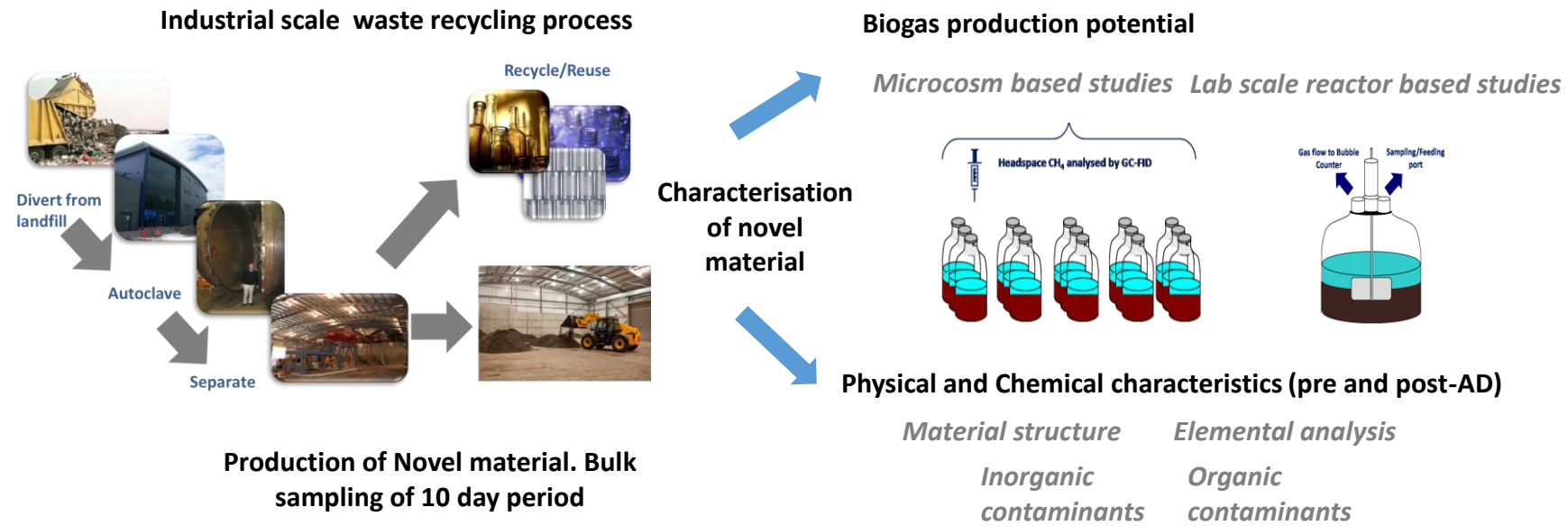


Figure 1. The industrial process (left) and approach to characterisation of this novel organic fibrous material (right)

Figure 2

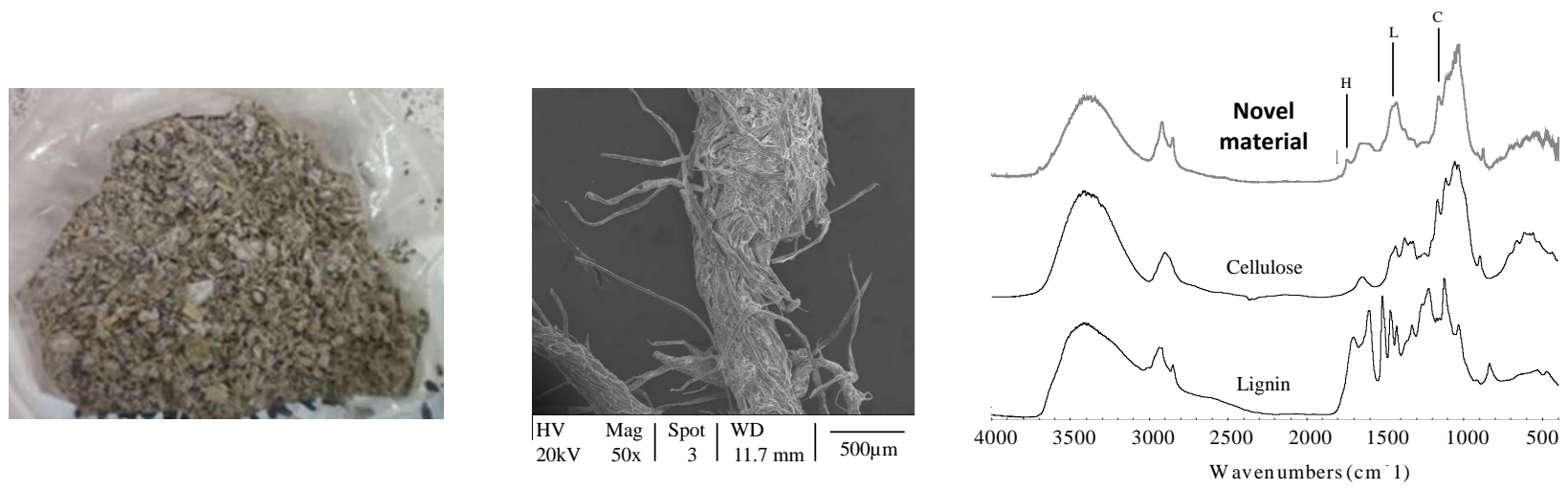


Figure 2. The visual appearance (left), structure as defined by SEM at a magnification of x 50 (centre), and composition of the novel organic fibrous material with respect to major carbon components using FTIR (right) compared with analytical grade cellulose and lignin.

Figure 3

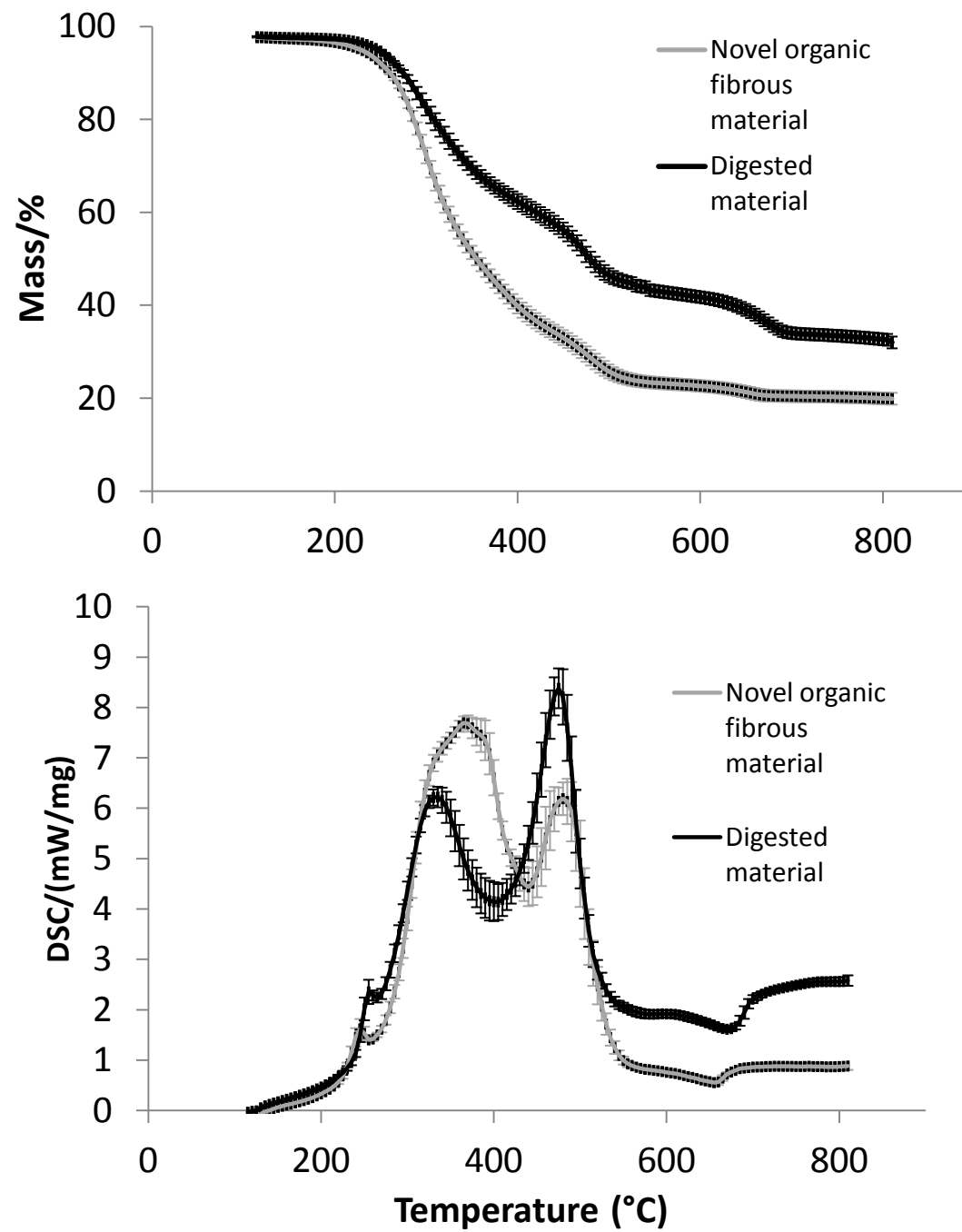


Figure 3. Average DSC (top) and TG (bottom) profiles of novel organic fibrous material and the resulting anaerobic digestate.

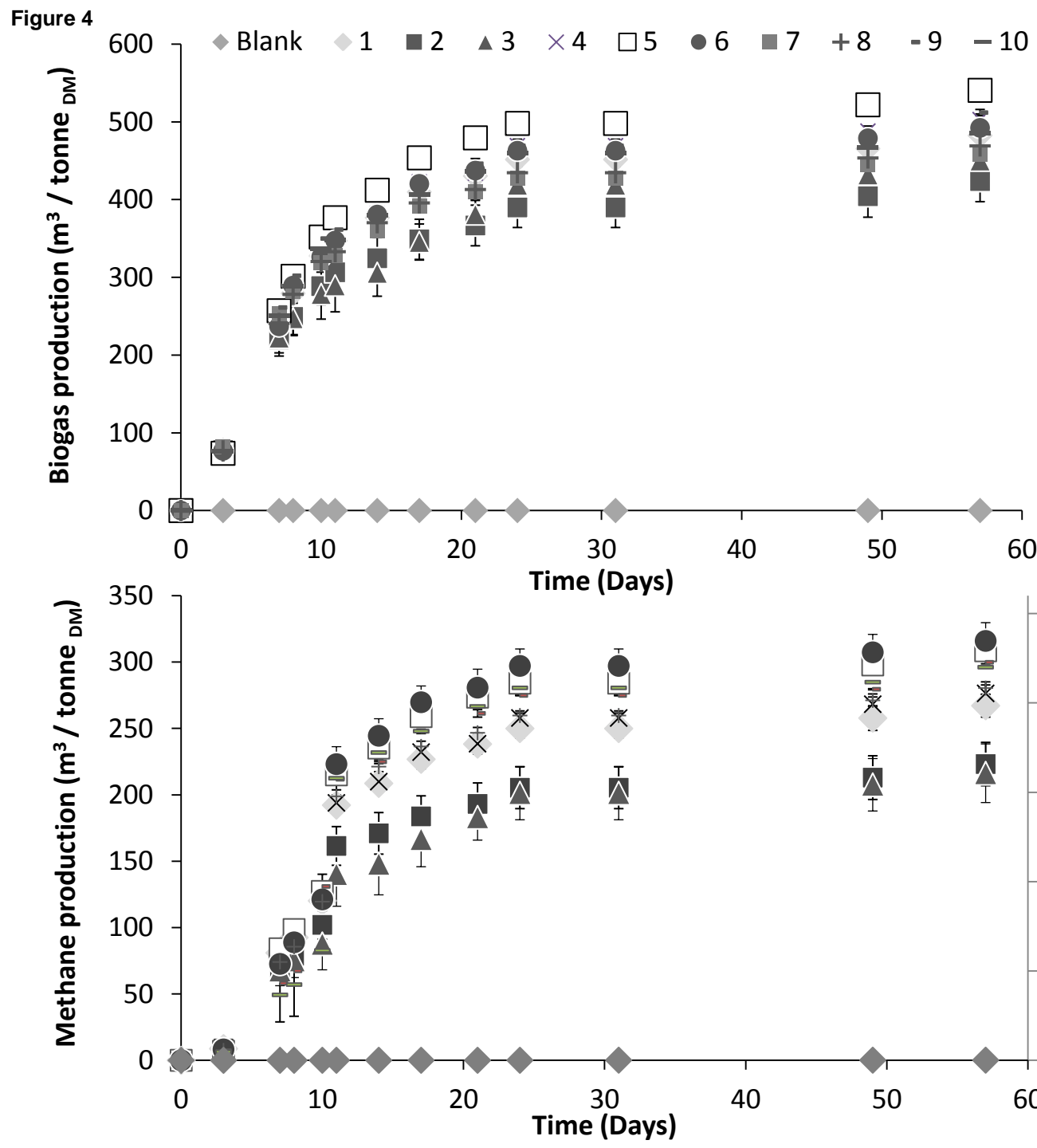


Figure 4. Biogas production ($\text{m}^3 / \text{tonne}_{\text{DM}}$; Top) and methane production potential ($\text{m}^3 / \text{tonne}_{\text{DM}}$; and $\text{M}^3 / \text{tonne VS}$ Bottom) from thermophilic batch microcosms (1-10). The blank contains inoculum only. In each instance error bars equal \pm standard error ($n=3$).

Figure 5

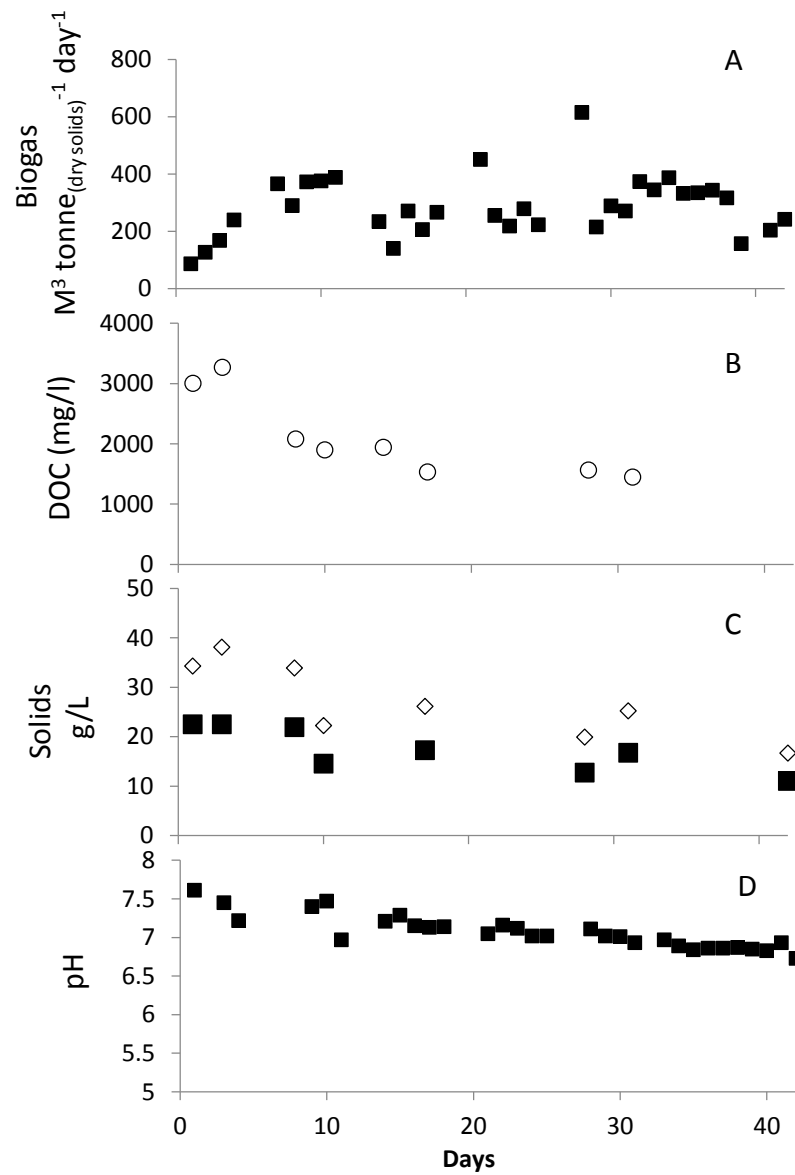


Figure 5. Performance of an AD reactor treating the MSW derived novel organic fibrous material: (a) biogas production rate per tonne added dry mass (black squares); (b) digestate dissolved organic matter (open circles); (c) digestate total suspended solids (open diamonds), digestate total volatile solids (closed squares); (d) digestate pH

Figure 6

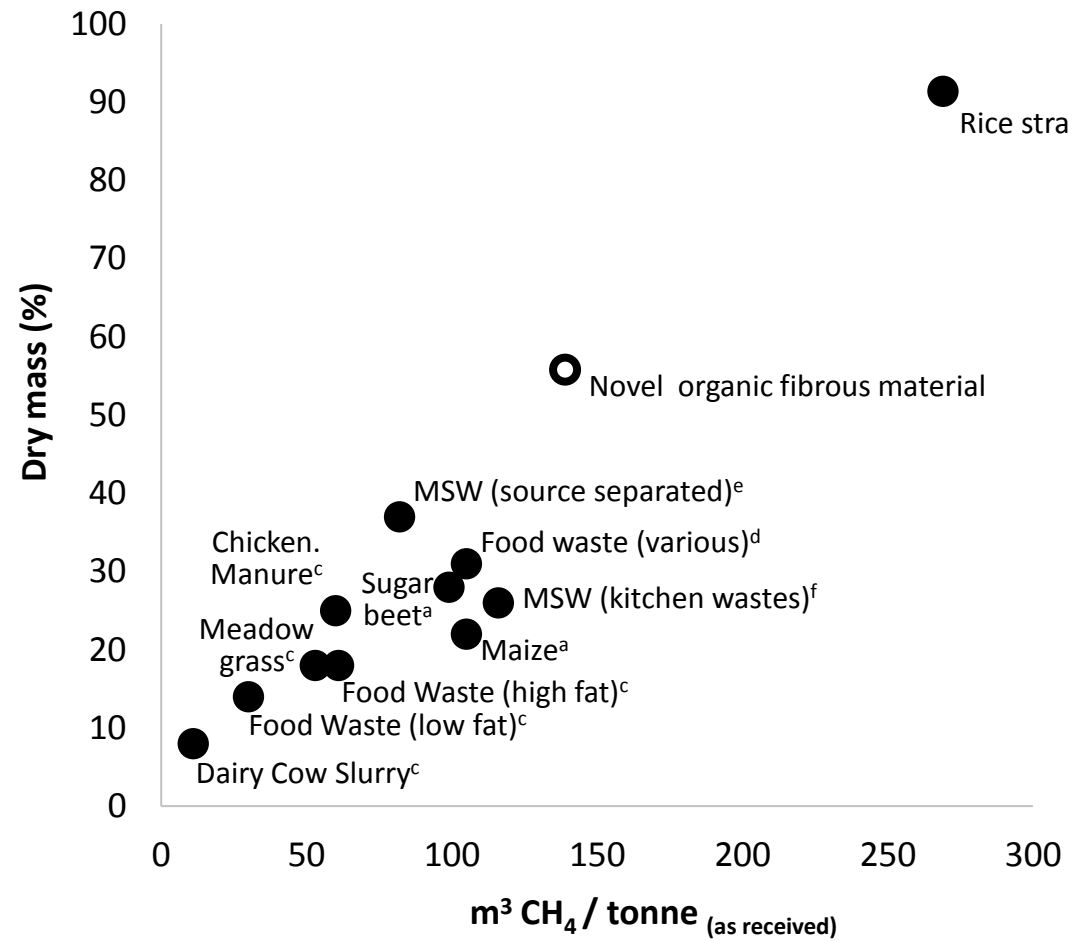


Figure 6. Comparison of methane production potential of our novel organic fibrous material with typical bio-solid and MSW derived AD feedstock's based on % dry Mass (source of data for each feedstock follows: ^aKWS, 2011, ^bPaepatung et al., 2009, ^cCROPGEN, 2004, ^dZhang et al., 2007, ^eMartín-González et al., 2010, ^fDavidsson et al., 2007).

Table 1

Table 1. Key physical and chemical characteristics of 10 sample batches of our novel organic fibrous material. Please note that: ¹where stated contaminants levels were below detection limits; ²one way ANOVA was carried out on three sets of triplicate data where available (sampling days 1, 3 and 9).

<i>Properties</i>	<i>Average value</i>	<i>± CI (set at 95%)</i>	<i>one way ANOVA*²</i>	<i>Regression analysis</i>
Total Moisture (%)	44.2	2.33	0.68	0.09
pH	7.1	0.25	0.33	0.53
C:N	32.9	3.46	n/a	0.49
Gross Calorific Value (MJ/Kg _(DM))	17.4	0.29	0.06	0.25
*%LOI ₅₅₀	74.1	4.06	0.38	0.88
<i>Elemental composition</i>				
% Carbon _(DM)	38.74	2.35	n/a	0.21
% Hydrogen _(DM)	4.69	0.44	n/a	0.64
% Oxygen - _(DM)	30.07	2.88	n/a	0.03
% Nitrogen _(DM)	1.19	0.10	n/a	0.67
% Sulphur _(DM)	0.27	0.04	n/a	0.39
<i>Contaminant content</i>				
Cadmium (mg/kg)	0.63	0.19	0.78	0.90
Chromium (mg/kg)	51.4	4.41	n/a	0.34
Copper (mg/kg)	56.3	7.45	n/a	0.62
Lead (mg/kg)	79.2	23.71	0.24	0.22
Mercury (mg/kg)	<0.3* ¹	n/a	n/a	n/a
Nickel (mg/kg)	28.9	5.17	0.12	0.87
Zinc (mg/kg)	202	44.5	0.12	0.27
Total PAH (mg/kg)	2.2	0.30	0.61	0.72
Total PCB (mg/kg)	<0.02* ¹	n/a	n/a	n/a

*%LOI₅₅₀ is equivalent to Volatile solids (VS)

Table 2

Table 2. Comparison of the heavy metal content of the novel organic material and its AD digestate (\pm CI 95%) with values for: background levels in soil; regulatory thresholds and standards for composts and digestates; source segregated and non-source segregated feedstocks; and single values presented for an autoclaved food waste.

Materials	Heavy metal content mg/kg_(DM)							Reference
<i>Soils and standard thresholds</i>	<i>Cd</i>	<i>Cu</i>	<i>Cr^{tot}</i>	<i>Hg</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>	
Median UK soil content	0.8	23	41	nd	25	74	97	McGarth and Cegarra (2006)
Median worldwide soil content	0.35	30	70	nd	50	35	90	Smith (2009)
EU range (Digestate thresholds)	0.7-6	70-1000	70-1000	0.3-16	20-350	45-750	200-4000	Saveyn and Eder (2014)
EU median (Digestate thresholds)	3.35	535	535	8.15	185	397.5	2100	Saveyn and Eder (2014)
EU (Sewage sludge thresholds)	20-40	1000 -1750	-	16-25	300-400	750 -1200	2500 -4000	European Commission (1986)
UK (Digestate thresholds)	1.5	200	100	1	50	200	400	BSI PAS 110 (2010)
Italian (Digestate thresholds)	3	300	N.A	3	100	280	400	Sharma et al (1997)
Germany (Digestate thresholds)	1.5	100	100	1	-	150	400	Saveyn and Eder (2014)
<i>Anaerobic Digestion feedstock materials</i>								
Novel organic fibrous material (n=10 sample days)	0.63 (\pm 0.19)	56.3 (\pm 7.45)	51.4 (\pm 4.41)	<0.3	28.9 (\pm 5.17)	79.2 (\pm 23.71)	202 (\pm 44.5)	current study
Autoclaved food waste (n=1)	0.76	2.61	nd	nd	0.64	nd	41.2	Ibrahim et al (2011)
House hold floc material (range, n= N.D)	0.31 - 6.50	61-92	20-86	<0.01-0.14	13-58	52-330	320-720	Papadimitriou et al (2008)
<i>Anaerobic Digestate materials</i>								
Digested novel organic fibrous material (calculated average) ^a	1.4	123.5	112.7	<0.3	63.4	173.7	443	current study
Digestate from MS AD composted MSW (n = N.D)	0.72	159	26	0.27	21	470	399	Smith (2009)
Digestate produced from Food Waste (mean, n= 6)	1.2 (SD = 0.8)	31.5 (SD = 8.5)	50.2 (SD = 54.2)	1.1 (SD = 0.06)	43.2 (SD = 54.2)	46.3 (SD = 42.7)	105.1 (SD = 24.7)	WRAP (2011)
Digestate from Animal slurry (mean, n = 14-40)	1.5 (SD = 0.5)	82.1 (SD = 47.8)	12.4 (SD = 7)	0.1 (SD = 0.2)	8.6 (SD = 4.5)	1.0 (SD = 3.4)	240 (SD = 115.7)	WRAP (2011)

^athe average metal contents of the digestate has been conservatively calculated based on an assumption that the metals remain in the digestate solids after a mass removal during AD of 54.4% (as indicated by TG-DSC analysis of samples before and after the AD process).

Table 3

Table 3. Comparison of biogas potential of our novel organic AD feedstock material with typical bio-solid and MSW derived AD feedstock's (source of data for each feedstock follows: ^aKWS, 2011, ^bPaepatung et al., 2009, ^cCROPGEN, 2004, ^dZhang et al., 2007, ^eAEBIOM, 2009 ^fMisty et al., 2008, ^gMartín-González et al., 2010, ^hDavidsson et al., 2007, ⁱCampuzano, R., Gonzalez-Martinez, S., 2016).

AD Feedstock	m ³ CH ₄ /tonne _(DM)	m ³ CH ₄ /tonne _(AR)	m ³ CH ₄ /tonne _(VS)	% CH ₄ in biogas	Dry matter (%)
Novel organic fibrous material	201-297	112-166	271-401	51-62	55.8 (± 2.33)
Sugar beet^a	412 -450	99	-	55	28-35
Maize^a	300-375	105	-	53	22-24
Rice straw^b	294	269	340	60	91.4
Food Waste_(high fat)^c	340	61	401	68	18
Food Waste_(low fat)^c	214	30	261	69	14
Dairy Cow Slurry^c	137	11	161	55	8
Meadow Grass^c	294	53	323	54	18
Chicken Manure^c	240	60	320	65	25
Food waste_(various)^d	340	105	440	73	31
Biowaste^e	-	100	-	61	-
MSW_(biodegradable)^f	75-150	-	-	60	-
MSW_(source separated)^g	221	82	298	63.2	37
MSW_(kitchen wastes)^h	271-470	70-155	298-573	60-62	26-33
OFMSWⁱ	-	-	300-600	-	19.6 – 34.8